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1 Structure and hydrogeochemical functioning of a sparkling natural mineral  
2 water system determined using a multidisciplinary approach: a case study  
3 from southern France

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11 ABSTRACT

12 Natural mineral waters (NMW), often used to produce bottled water, are of high socio-  
13 economic interest and need appropriate management to ensure the sustainability of the  
14 resource. A complex sparkling NMW system at La Salvetat, southern France, was  
15 investigated using a multidisciplinary approach. Geological and geophysical investigations,  
16 pumping test analyses, time-series signal processing, hydrogeochemical and isotopic data (both  
17 stable and radiogenic), and numerical modelling provided complementary information on the  
18 geometry, hydrodynamic characteristics and functioning of this mineral system. The conceptual  
19 model consists of a compartmentalized reservoir characterized by two subvertical, parallel deeply-  
20 rooted hydraulically independent permeable structures that are fed by deep CO<sub>2</sub>-rich crustal  
21 fluids. The non-mineralized shallow aquifer system corresponds to a fissured layer within the  
22 weathered zone that is recharged by leakage from the overlying saprolite. This surficial aquifer  
23 responds rapidly to recharge (40-80 days), whereas the deep system's response to recharge is  
24 much longer (up to 120 days). This research demonstrates the need for multidisciplinary

25 approaches and modelling (quantity, hydrochemistry) for understanding complex NMW systems.  
26 This knowledge is already being applied by the bottling company that manages the resource at  
27 La Salvetat, and would be useful for conceptualizing other NMW sites.

28

29 Keywords:thermal conditions, CO<sub>2</sub>, fractured rock, natural mineral water, France

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## 36 1. INTRODUCTION

37 Sparkling natural mineral waters, and more generally natural mineral waters (NMW),  
38 often used to produce bottled water, are of socio-economic interest. In order to sustain these  
39 resources, appropriate management is needed that is well informed by local hydrogeological  
40 understanding.

41 Hydrothermal systems comprise the following three main geological components: water,  
42 heat and permeability(Clemente and Villadolid-Abrigo 1993; Lachassagne et al. 2009).  
43 Sparklingnaturalmineral water systems comprise water, CO<sub>2</sub> and permeability so water and gas  
44 can flow and rise to the land’s surface. Geogenic CO<sub>2</sub>may originate from three sources:  
45 metamorphism of carbonate rocks in the Earth (Kerrick and Caldeira 1998), transformation of  
46 organic matter during oil, gas and coal formation (Battani et al. 2000), or degassing of the  
47 mantle(Shipton et al. 2005). Consequently, in most cases, CO<sub>2</sub> is of deep origin. In crystalline  
48 rocks, deep fractures create the required permeability to bring the CO<sub>2</sub> to the surface, often as  
49 springs. At a relatively shallow depth (tens to hundreds of meters), these structures also  
50 constitute the drilling targets for safely abstracting the NMW. Therefore, the identification of the

51 geometry, hydrodynamic properties, extent(both laterally and with depth), and thickness of such  
52 permeable structures are the key factors for correctly understanding, tapping, managing, and  
53 protecting the mineral water system.

54 In crystalline rocks, the hydrodynamic properties of shallow (0-100 m) aquifers, and their  
55 relationships with weathering processes are now well characterized, with comprehensive  
56 conceptual models (Dewandel et al. 2006; Dewandel et al. 2011; Lachassagne et al. 2011).  
57 Deeper, nuclear waste storage projects have achieved very precise characterization of the (low  
58 permeability) fractured network of crystalline rocks, but in areas specifically chosen to avoid  
59 deep fracturing (Gustafson et al. 2009; Morosini and Rhen 2000). Thus, it appears that the  
60 precise characterization of deep permeable structures is very rare, and often based on  
61 conjecture and/or uncertain assumptions. This research is devoted to characterizing such  
62 complex NMW structures.

63 Another objective of the research was to show that such complex natural mineral water  
64 systems require multidisciplinary approaches, combining several techniques, in order to propose  
65 an appropriate precise, realistic and robust conceptual model to tackle this complexity. The  
66 approach used combines geological, geophysical, hydrodynamic and times series analysis,  
67 hydrogeochemical and isotopic data, and a comprehensive numerical model in order to  
68 characterize and simulate the permeable reservoir of a NMW system in crystalline rocks. This  
69 approach is applied to the La Salvetatsparklingnatural mineral water system in southern France  
70 which is bottled. The knowledge about the structure and functioning of this mineral water system  
71 is of high interest for the bottling company for the development, sustainable management and  
72 protection of its spring. Developing a realistic conceptualization for a well characterized site is  
73 also of broad interest in order to inspire conceptualizations of other NMW sites.

## 74 2. STUDY AREA

75 The sparkling water spring at La Salvetat (Hérault region, southern France) has been  
76 known at least since the Middle Ages, particularly by the Santiago de Compostella pilgrims who  
77 rested and bathed at the Rieumajou spring. The spring has been operated for NMW bottling by  
78 the Danone group (Evian Volvic World Sources, Danone Waters France) since the early 1990s,  
79 and is now, together with forestry and traditional mountain agriculture, one of the key drivers of  
80 the local economy and employment. This NMW spring emerges in a bedrock region composed  
81 primarily of metamorphic rock without obvious visible tectonic structures at the surface. The field  
82 is located south of the Raviège hydropower lake dam within the large south eastern France CO<sub>2</sub>  
83 region (an area where numerous carbonate-rich springs occur), which is part of the larger CO<sub>2</sub>  
84 Alpine foreland (Blavoux and Dazy 1990). The reservoir is currently exploited by six wells (B1,  
85 R1, R2, R3, R5 and R6, **Erreur ! Source du renvoi introuvable.**). Observation boreholes (R4  
86 inoperative well, P1, P3, MLC2, ML3, Pz1 to 7) are used for reservoir monitoring. Recently, five  
87 new cored 200 m-long exploration boreholes were drilled (HF1 to HF5). The data from numerous  
88 older wells, now closed, are also available.

89 The local climate is predominantly Mediterranean with a strong mountainous  
90 (“Cévenole”) influence. During the 1993-2008 period, the mean annual rainfall was 1,444 mm  
91 with a mean annual potential evapotranspiration of 806 mm. A reservoir model (Ladouche et al.,  
92 BRGM, unpublished data, 2013), calibrated using the daily time series of shallow aquifer water  
93 table fluctuations (water supply Port well) and runoff (at the 48 km<sup>2</sup> Agout River crystalline  
94 watershed scale), provides estimates of effective rainfall (920 mm/yr), recharge to the shallow  
95 aquifer (169 mm/yr) and runoff (751 mm/yr).

### 96 3. METHODOLOGY

97 The multidisciplinary approach, implemented to characterize the permeable reservoir of  
98 La Salvetat NMW field, comprised four stages. The first involved a detailed geological study  
99 (lithology, weathering, sequence stratigraphy, structural geology, fissure and

100 fractureidentification) and a field hydrogeological study. The geological approach combined a  
101 pole-dipole geophysical survey(14 mostly north-south profiles with an investigation depth of  
102 about 120 m totaling about 16.5 km performed in 2011 - Figure 1), and geological field  
103 investigation, involvinga comprehensive survey of the outcrops and their comparisonto local  
104 lithotypes to complement the 1:50000 scale BRGM geological map (Demange et al. 1995). The  
105 geological field investigation also comprised the geological reinterpretation of all available cores  
106 (11 boreholes), cuttings (3 boreholes), and existing geological logs for thoseboreholes where the  
107 cuttings and cores were no longer available, along with macroscopic and microscopic (thin  
108 section) analysis. In the studied area (Fig. 1), due to the weathering, the outcrops are small in  
109 size (less than a few square meters), and mostly restricted to granite veins that appear to be  
110 less weathered than the nearby geological formations. There the fracturing is mostly linked to  
111 weathering processes.

112         The field hydrogeological approach was primarily focused on characterizing the springs  
113 (fresh water and NMW), particularly during the La Raviègelake's low water-level period.To  
114 characterize the hydrodynamic properties of the aquifer, pumping tests and interference tests  
115 between production wells wereanalyzed. The interpretation of pumping tests in crystalline  
116 aquifers is a difficult task, as groundwater flow can be fractionalized (Black 1994), ie. controlled  
117 by the hydraulic conductivity of fractures, fracturedensity and orientation, their relationship with  
118 the low-hydraulic-conductivity blocks or matrix (Maréchal et al. 2004), and the geometry of the  
119 faults or intrusive bodies acting as permeable or impervious structures (Dewandel et al. 2011).  
120 To reveal the various aspects of the hydrogeological properties of such a complex  
121 hydrogeological system, and particularly the geometry of fractured zones tapped by NMW  
122 pumping wells, careful attention was paid to diagnosing the test responses prior to modelling  
123 with an analytical solution. Diagnoses were based on the analysis of derivative drawdown curves  
124 on log-log plots, which allows flow-regime identification (Ehlig-Economides 1988; Renard et al.  
125 2009). According to the results of the diagnosis, suitable analytical models for partitioned(Nind

126 1965) or leaky aquifers (Hantush 1960) were used in order to calculate the hydrodynamic and  
127 geometric parameters of the aquifer.

128 The hydrogeological processes were characterised using a signal processing method  
129 applied to the rainfall, piezometric level and fluid electrical conductivity time series. The functions  
130 used (autocorrelation and cross-correlation) and their corresponding mathematical expressions  
131 have been described by several authors (Mangin 1984). An analysis methodology was also  
132 developed in this study to extract recharge information from the measured signal, disturbed,  
133 amongst others factors, by pumping, thereby providing quantitative information on the recharge  
134 rate and the dynamics of its transfer function. Piezometric and electrical conductivity variations  
135 (O: system output) were explained by considering the input variables likely to influence the  
136 system. This involved describing a Multiple Input Single Output (MISO) system (Kothyari and  
137 Singh 1999). The calculations were performed using the Tempo software with a one-day time  
138 step (Pinault et al. 2001).

139 Water chemistry and isotopic tracing (stable isotopes of water, strontium) were used in  
140 order to constrain the hydrochemical mechanisms and to understand the origin of the mineral  
141 waters system. The pH, temperature and electrical conductivity were measured onsite on raw  
142 water samples. Samples for cation, trace metallic element and Sr isotope determination were  
143 filtered through 0.45  $\mu\text{m}$  Millipore membrane filters and acidified (with ultrapure  $\text{HNO}_3$  to  $\text{pH} < 2$ ).  
144 Anions were determined by ion chromatography; cations and trace elements by ICP-MS. The  
145 measurement uncertainties for major and trace elements are 5 and 10%, respectively. Oxygen  
146 ( $^{18}\text{O}$ ) and hydrogen (D) isotope measurements were done with a standardized method, using a  
147 Finnigan MAT 252 mass spectrometer with a precision of  $\pm 0.1\text{‰}$  vs SMOW for  $\delta^{18}\text{O}$  and  $\pm 0.8\text{‰}$   
148 for  $\delta\text{D}$ . The  $^{18}\text{O}/^{16}\text{O}$  ratio is reported as  $\delta$  deviation (per mil) of this ratio in the sample from that  
149 of the V-SMOW standard. Isotopic compositions are reported in the usual  $\delta$ -scale in  $\text{‰}$ . Analysis  
150 of the  $\delta^{13}\text{C}$  composition of the  $\text{CO}_2$  was done by mass spectrometry with a precision of 0.1  $\text{‰}$ . The  
151  $^{13}\text{C}/^{12}\text{C}$  ratio is expressed in per mil notation relative to standard V-PDB. In addition, strontium

152 isotope analyses on the main rocks and mineral phases were performed to better understand  
153 water-rock interactions. The objective was to define the isotopic signatures for strontium  
154 ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) in the main rocks comprising the La Salvetat reservoir in order to interpret the origin  
155 and variations in the isotopic strontium ratio in the sparkling NMW field. Chemical purification of  
156 Sr (~3  $\mu\text{g}$ ) was done using an ion-exchange column (Sr-Spec) before mass analysis according  
157 to a method adapted from (Pin and Bassin 1992), with total blank <1 ng for the entire chemical  
158 procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament  
159 with a tantalum activator and analysed with a Finnigan MAT 262 multi-collector mass  
160 spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194. An average  
161 internal precision of  $\pm 10 \times 10^{-6}$  ( $2\sigma$ ) was obtained and the reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
162 measurements was tested by repeated analyses of the NBS987 standard, for which a mean  
163 value of  $0.710230 \pm 18 \times 10^{-6}$  ( $2\sigma$ ,  $n=12$ ) was obtained.

164 To determine the theoretical isotopic signature of water interacting with a given rock, a  
165 theoretical dissolution model must be used (Bullen et al. 1997). Such a dissolution model has  
166 been developed (Negrel et al. 2001) assuming that most of the Sr released by weathering  
167 comes from the following three main minerals: plagioclase, K-feldspar and biotite. Model  
168 parameters are: (i) Sr content in the main mineral phases (plagioclase, K-feldspar and biotite),  
169 (ii) their isotopic Sr composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ), (iii) the proportion of each of these minerals in the  
170 studied rock and, (iv) the weatherability of each of these minerals (Petelet Giraud et al. 2003).  
171 The total rock sample and separate minerals were analysed for Rb and Sr content and  $^{87}\text{Sr}/^{86}\text{Sr}$   
172 isotopic ratio. The separation of K-feldspars, plagioclases and biotite was performed by particle-  
173 size (on the 50-400  $\mu\text{m}$  fraction), densimetric (K-feldspars, plagioclases and part of biotite) and  
174 magnetic separation (rest of biotite). The nature of the plagioclases was analysed by electronic  
175 microprobing: they can be classified as oligoclase (An<sub>90-70</sub>Ab<sub>10-30</sub>) and andesine (An<sub>30-</sub>  
176 <sub>50</sub>Ab<sub>70-50</sub>). Calcite separation in the Cipolin marble sample (R6 149.1) was performed by rock

177 stripping (thin sections and hand samples) using a microgrinder. The results of these dissolution  
178 models were then compared to the water samples from the wells to explain their origin.

179 Finally a hydrodynamic and reactive hydrogeochemical numerical model was developed  
180 to dynamically simulate the functioning of the NMW system. It was used to integrate all the  
181 information provided by the multidisciplinary study, and to validate the conceptual model. The  
182 modelling method selected is the networked reservoir and chemical reactor methodology (Collon  
183 et al. 2002). It is based on the main assumption that piezometric levels and chemical  
184 concentrations are uniform within each reservoir. The system modelled is then described by a  
185 set of ordinary coupled differential equations translating water storage and chemical elements in  
186 each of the variable volume reactors. The water-rock interactions were taken into account by  
187 introducing aqueous phase chemical kinetics for certain reactive chemical elements. The  
188 relevance of the model to reflect the system studied lies in the choice of the number of  
189 reservoirs, the way they are connected, the laws chosen to describe the water and matter  
190 exchanged amongst the reservoirs, and the choice of the reactive chemical elements and the  
191 related chemical kinetics.

## 192 4. RESULTS

### 193 4.1. GEOLOGICAL STRUCTURE OF THE MINERAL WATER SYSTEM

194 The detailed geological approach confirmed the overall high quality of the 1:50000  
195 geological mapping (Demange et al. 1995) in the Rieumajou spring area. The main  
196 lithotypes were observed in the field and their distributions were well contoured, at least at the  
197 scale of the map. The bedrock in La Salvetat area is mostly composed of intensely folded and  
198 foliated metamorphic rocks derived from a sedimentary sequence overlying a more ancient  
199 granitic substratum. In the mineral spring area, this series exposes, from South to North, a  
200 conformable succession, from bottom (South) to top (North) (**Erreur ! Source du renvoi**

201 **introuvable**): (i) the Larnorthogneiss derived from a Cadomian granite metamorphosed during  
202 the Hercynian orogeny, and weathered prior to being covered by sediments and prior to being  
203 further metamorphosed; (ii) a Cambrian sedimentary sequence lying unconformably on the  
204 metamorphosed granite, and consisting of four main geological formations:

205  
206 1) a 50 to 100 m thick schist-quartzite Puech-Plô grey gneiss composed of ancient,  
207 coalescent and detritic deltas aligned perpendicularly at contact between the ancient  
208 basement and the paleo sedimentary series;

209 2) a 20 to 30 m thick quartzo-feldspathic Murat gneiss, a metamorphosed volcanic-  
210 sedimentary formation (conglomerates, leptynites) infilling the lowest points between the  
211 paleodeltas;

212 3) a more than 100 m thick Nagesparagneiss rich in calcic levels: plagioclase-rich gneiss,  
213 gneiss with calcic silicates and Cipolin marbles. This series is a prograding-retrograding  
214 platform which, in top parts is mostly carbonated. It shows a typical Klüpfelian carbonated  
215 deposit profile which provides a distal deeper facies, probably located at the south  
216 towards a coastal proximal located at the north with the following geological facies: clay-  
217 rich siltites, carved aggrading alternations from a subsiding bay, coastal prograding  
218 alternations, tidal dunes, beach, and intertidal stromatolites. The analysis of the  
219 sedimentary signal shows that this carbonated platform series is transgressive on the  
220 Puech-Plô and the Larn Gneiss formations. In several wells, this series is duplicated with  
221 first (near the surface) the inverted series, and then the normal one. Moreover, the  
222 resulting inversion line (and also the series) is folded.

223 4) Late hercinian granite and pegmatite intrusive veins (tourmaline leucocratic granite  
224 and pegmatite).

225 The foliation is mostly N050 to 090°E (Figure 2). The units dip at 70 to 80° South to North;  
226 consequently, these geological formations are considered to be deeply rooted and are still  
227 crosscut in the boreholes at depths greater than 200 m.

228 The main outcome of the detailed geological mapping concerned the granite veins. The  
229 authors of the 1:50000 geological map inferred that these veins resulted from the partial melting  
230 of the other lithological units during metamorphism, and consequently, that they are conformable  
231 (same dip) with the main foliation of the lithological units and effectively are sills “invading” the  
232 other lithological units. However, the field survey clearly showed that the granite is much  
233 younger and occurs as subvertical, N110 to N160°E oriented veins that are meters to tens of  
234 meters thick and tens to hundreds of meters long. These veins are not conformable with the  
235 other rocks as they cross-cut all the other lithologies (Figure 2).

236 These formations are deeply weathered with an up to 30 m thick cover of unconsolidated  
237 saprolite. Differential weathering has resulted in higher relief granite veins (with several  
238 outcrops), whereas the Nages formation rocks outcrop only very locally. As a consequence, in  
239 the spring area, the outcrops are quite poor and do not allow performing a detailed structural  
240 analysis. As far as faults can be identified on cores, the drillings crosscut several fracture zones  
241 which mostly seem to be dilational (no compressive tectoglyphs). Several fractures comprise  
242 breccias that in places are cemented with calcite and/or silica and can show signs of  
243 hydrothermal activity. It was possible to characterize the orientation and dip of 15 open or  
244 mineralized fractures observed on the cores. These fractures were oriented, using the foliation  
245 measured in the well as a geometric reference. The following main results were obtained:  
246 fracture orientation in the wells is mostly N100-110°E (n = 9), and then N130-140°E (n = 3), and  
247 N020-030°E (n = 3).

248 Electrical profiles (survey lines shown in Fig. 1) clearly reveal the depth of the weathering profile.  
249 Typically, the electrical resistivity is below 1000 Ω.m within the first 50 m below ground surface  
250 (Figure 3). There is a sharp resistivity contrast at approximately 50 m, where the resistivity

251 increases to more than 5000  $\Omega$ .m, which can be followed within most of the Nages formation in  
252 Fig. 3 (M profile from X = 160 to 550 m and C profile from X = 120 to 340 m, and X = 600 to 840  
253 m). In these profiles, the thickest granite and pegmatite veins appear as more resistant (higher  
254 electrical resistivity) bodies within the low resistivity weathering profile (X = 480 m on the M  
255 profile). However, apart from this result about some granite veins, the electrical profiles do not  
256 provide unambiguous information about the lithology, notably below the weathering profile. The  
257 electrical profiles also reveal enhanced weathering (or past hydrothermalism) along some  
258 lithological contacts, particularly the southern Puech-Plô/Murat and Nages contact (subvertical,  
259 about 150 m wide - locally much wider - 50 to 70  $\Omega$ .m structure that can be followed on most of  
260 the North-South electrical profiles; Fig. 3 - M profile from X = 90 to 155 m and C profile from X =  
261 60 m to 120 m). The most interesting results from the geophysical survey are the deep (more  
262 than 100 to 120 m) subvertical conductive structures (locally down to about 10  $\Omega$ .m, but more  
263 frequently between 150 and 200  $\Omega$ .m; Fig. 3 - M profile from X = 550 m and C profile from X =  
264 340 to 480 m). These structures are 30 to more than 50 m wide, are oriented N100-110°E, and  
265 coincide with the fractured zones in wells producing NMW (see the dotted blue curves on Figure  
266 2). One of these structures, the southern one, identified on five North-South electrical profiles,  
267 seems to link the R4 area (West) at least to HF4 and B1 wells (East). The second structure, the  
268 northern one, only identified on two profiles due to the presence of the lake (which limited the  
269 geophysical measurements), links the area of R5 (West) with the HF2 area (East). These  
270 structures (HF2, HF4 boreholes) and some other conductive anomalies (HF1, HF3, HF5  
271 boreholes) were targeted during the last drilling campaign, and only the HF2 and HF4 boreholes  
272 successfully tapped permeable NMW bearing fracture zones in the "southern" and "northern"  
273 structures.

274

#### 275 4.2. PRELIMINARY HYDRODYNAMIC APPROACH

276 The synthesis of blowing discharge measurements performed during down-hole-hammer  
277 drilling shows that the fissured zone of the Puech-Piô formation is much less productive than the  
278 Nagesformation, with mean discharges 3 to 4 times lower. The productivity of the Nages  
279 formation is nearly nil within the saprolite (first 20 to 30 meters below ground surface) and is  
280 relatively higher within the underlying 30 - 40 m thick fissured zone. Productivity is nil within the  
281 deeper unweathered rock, except where the borehole crosscuts a deep NMW bearing fracture.

282 Piezometric measurements available from the wells tapping the NMW bearing fractures  
283 show two East-West slight piezometric depressions corresponding to the two structures  
284 identified from geological and geophysical data (Figure 1). These depressions appear to be  
285 related to the natural flow within the mineral aquifer and to the pumping in the wells. The first  
286 piezometric depression extends from R4 to R1 (pumping in R1, R2, R3). The second one  
287 corresponds to R5 and R6 pumping. Most of the formerly flowing or still-existing NMW springs  
288 appear to be located at the intersection between the two East-West structures and the  
289 topographical low points (**Erreur ! Source du renvoi introuvable.** and **Erreur ! Source du**  
290 **renvoi introuvable.**). One main location is West of each structure, at their lowest topographical  
291 point. The second one is a small North-South valley in the vicinity of R1 and R2 wells where the  
292 main NMW spring was located. There is no significant NMW outflow in the HF4-B1 area, which  
293 is interpreted as a consequence of the low permeability of the geological cover in this valley, as  
294 piezometric levels in the mineral aquifer in that area are aboveground level. Consequently, from  
295 these data, it can be inferred that the natural mineral water may have flowed naturally  
296 (i) upwards and then westward from the B1 area toward the main NMW spring (between R1 and  
297 R2) and then to R4, and (ii) from R5 (or even from HF2) to the springs located east of R6.

#### 298 4.3. HYDRODYNAMIC PARAMETERS AND AQUIFER STRUCTURE FROM PUMPING TESTS

299 Data from 30 pumping tests, a few hours to several months in duration, and performed on  
300 ten of the Rieumajou area wells were interpreted to establish interferences between the wells,

301 and to evaluate the geometry of the permeable formations and their hydrodynamic parameters.  
302 Except well R5, in which the screened part mainly crosscuts a granite vein, all others are sited  
303 within the Nages gneiss. The tests were performed between 1990 and 2011 at the time of well  
304 drilling. During the pumping tests, water level changes in nearby wells and piezometers were  
305 also observed.

306 One example of a 10-day pumping test performed on well R4 in 2010 is presented (**Erreur !**  
307 **Source du renvoi introuvable.**). R4 is 63.3 m deep and screened between 46.2 and 57.0 m  
308 into the NMW bearing fractures. The derivative curve is complex, but illustrates various typical  
309 flow regimes (**Erreur ! Source du renvoi introuvable.**):

- 310 - from the beginning of the test to 20 minutes duration describes the wellbore storage  
311 effect,
- 312 - from 20 to 50 minutes, the flat trend of the derivative curve is typical of infinite radial flow  
313 from which aquifer transmissivity can be calculated ( $T=5.4 \times 10^{-4} \text{ m}^2/\text{s}$ ),
- 314 - from 50 to 400 minutes, the derivative curve tends to a  $\frac{1}{2}$  slope, and the drawdown  
315 reaches two parallel no-flow boundaries,
- 316 - from 400 to about 6,000 minutes, the derivative curve follows a unit slope typical of  
317 bounded aquifers (at least two additional no-flow boundaries),
- 318 - finally, from 6,000 minutes to the end of the test, drawdown tends to stabilize, and the  
319 decrease of the derivative suggests leakage from shallow aquifers. Such a leakage effect  
320 was only observed in this well.

321 This diagnostic shows that R4 is located in a bounded aquifer, the boundaries of which  
322 are close to the well (between 50 and 400 minutes). In addition, the aquifer is connected to  
323 another aquifer (most probably the shallow aquifer) by leakage: consequently, this well is not  
324 exploited, as pumping might induce shallow aquifer water inflow. This test was interpreted using  
325 a rectangular aquifer model with seepage (Hantush 1960) with four orthogonal no-flow

326 boundaries, wellbore storage effect and well skin(**Erreur ! Source du renvoi introuvable.** -  
327 black curves). The evaluated aquifer surface is 0.09 km<sup>2</sup> (about 400 m length by 200 m wide).

328 Test diagnosis and modelling were carried out to interpret the 29 other pumping tests, the  
329 main results of which are summarized in **Erreur ! Source du renvoi introuvable.** and Table 1. In  
330 summary, the interference tests clearly demonstrate that the site is partitioned into two  
331 approximately East-West direction compartments: a northern one (R5 and R6) and a southern  
332 one (R1-R2-R3-R4-P3-DAC). This result is supported by most of the test diagnoses. It is also  
333 highly consistent with the geophysical and piezometric data. Diagnostic and pumping test  
334 modelling also provide information about the aquifer geometry. The southern compartment is  
335 characterized by a permeable (fractured) zone, about 0.1 km<sup>2</sup> area (200x400 m approximately)  
336 and oriented in a near East-West direction (N105°E). Its eastern limit, however, is not well  
337 constrained. Its transmissivity is about  $3 \times 10^{-4}$  m<sup>2</sup>/s and is relatively constant from one well to  
338 another. Its storativity is about  $5 \times 10^{-4}$ . The northern compartment is also elongated in a near  
339 East-West direction and is probably smaller than the southern one; however, pumping tests  
340 were not long enough to reach all the boundaries. Transmissivity is similar to that of the southern  
341 compartment, but storativity is less,  $2 \times 10^{-5}$ .

342 Two of the pumping tests, at B1 and HF4, could not demonstrate any interference  
343 despite seeming to belong, geometrically and geologically, to the eastern continuation of the  
344 southern compartment. Nevertheless, interferences show that the two wells belong to the same  
345 fractured system ("B1" compartment). HF4 yielded a high transmissivity ( $8 \times 10^{-3}$   
346 m<sup>2</sup>/s) corresponding to a zone a few meters wide. The geometry of compartment B1 is not well  
347 constrained, but from pumping tests, two parallel no-flow boundaries are reached relatively late  
348 after the start of the pumping (3 000 min). This leads to the interpretation of an apparently  
349 (depending on assumption on S) very large fractured zone (about 800 m wide); the orientation of  
350 this fractured zone was not constrained by the modelling of the pumping tests, but it was by the

351 geophysical data. As discussed below (section '*Multiple input single output*'), the piezometric time  
352 series analysis confirms that the HF4-B1 compartment is the eastern prolongation of the R4-R1  
353 compartment.

354 Several pumping tests show evidence of partial penetration (Table 1), suggesting that the  
355 fractured zone extends much deeper than the bottom of the wells, which generally do not exceed  
356 100 to 120 m depth.

#### 357 4.4. HYDROGEOLOGICAL FUNCTIONING OF THE SYSTEM FROM TIME SERIES ANALYSIS

##### 358 4.4.1. PRELIMINARY DESCRIPTION OF HYDROLOGICAL TIME SERIES

359 Flow rate variations in the pumping wells (**Erreur ! Source du renvoi introuvable.**b)  
360 generally follow the same pattern, i.e., because of the constraints dictated by NMW production,  
361 flow rates are all increased or lowered synchronously. Very few periods exist in which differential  
362 flow rate variation is available.

363 Piezometry trends measured at R5 in the northern compartment show a correlation with  
364 lake water level, which, according to dam management records, is low during the winter energy  
365 production season and high in summer during the tourist season. For R6, time series are too  
366 short to provide a basis for conclusion. The head in the aquifer is thus affected by the surface  
367 hydraulic head imposed by the lake surface. At daily time scale, piezometric fluctuations at R5  
368 are impacted by pumping but it is not possible to identify whether this is only due to pumping at  
369 R5 or also at neighbouring wells. The very short-term piezometric fluctuations are due to the high  
370 quadratic (non-linear) head losses in the R5 well visible in 2004 and 2008-2009 when pumping  
371 rates are variable. Piezometric variability therefore appears to be essentially controlled by  
372 pumping rates and by variations in the lake water level, while piezometric variations linked to  
373 rainfall (recharge) appear to be negligible on short- and mid-time frames (several days to several  
374 weeks).

375 Piezometric trends in wells located to the South (R1, R2 and R3) do not appear to be  
376 influenced by water level variations in the La Raviègelake. Piezometric trends at R1 and R2 are  
377 very comparable, which confirms the existence of a hydraulic link between the two wells.  
378 Piezometric time series for R3 also show similar trends to those measured at R1 and R2. The  
379 piezometric variations appear to be controlled by pumping rate variations. Here again, these  
380 piezometric variations are primarily linked to high quadratic head losses. In a similar way to R5,  
381 piezometric variations induced by recharge are hidden in the short- (several days) and mid-  
382 timeframes(several weeks) by variations induced by pumping.

383 For several years after being put into operation (see R5, R6 and B1 because R1, R2, R3  
384 data were not recorded for the first years of service), all wells show an initial decrease in  
385 electrical conductivity (EC) over a period spanning several years (**Erreur ! Source du renvoi**  
386 **introuvable.**). EC then becomes relatively stable and shows variations with a shorter  
387 wavelength. Annual fluctuations in EC at R5 are in the range of 100  $\mu\text{S}/\text{cm}$ ; the annual  
388 amplitude appears to be relatively synchronous with lake level variations: maximum EC levels  
389 correspond to high water levels in the lake. Short-term pumping variations do not cause a  
390 significant variation in the EC of pumped water. The gradual increase in pumping rates at R5 in  
391 2009 (from 1 to 1.8  $\text{m}^3/\text{h}$ ), and again in 2010 (up to approximately 1.9  $\text{m}^3/\text{h}$ ), seems to cause a  
392 decrease in EC, as it did when the well was put into production (with R6 being put into  
393 production in 2009, overall pumping in this compartment reached nearly 4  $\text{m}^3/\text{h}$  as of 2010). In  
394 the other wells (R1, R2, R3 and B1), the EC does not appear to be controlled by lake water level  
395 fluctuations. Long-term oscillations observed in B1, R1 and R2 are explained below.

#### 396 4.4.2. CROSS CORRELATION ANALYSIS

397 Cross-correlation analysis involved three input variables: rainfall (P), lake water level ( $H_{\text{Lake}}$ )  
398 and the aggregate flow rates at wells ( $Q_x+Q_y$ ). Output included piezometry (H-well) or water  
399 mineralisation - EC, which is primarily controlled by  $\text{HCO}_3$  and calcium content (**Erreur ! Source**

400 **du renvoi introuvable.**a, b and c). Rainfall-piezometry cross-correlograms (**Erreur ! Source du**  
401 **renvoi introuvable.**a) are very noisy and show very low cross-correlation coefficients ( $<0.1$ )  
402 indicating that the rainfall signal is highly filtered/dampened by the system. Maximum correlation  
403 is observed for offsets ranging from 80-120 days. The shape of rainfall-piezometry cross-  
404 correlograms provides an approximation of recharge impulse response; it is indicative of  
405 hydraulic transfer within a weakly diffusive system. The end of the recharge impulse response  
406 occurs at an offset of approximately 250 days. The memory effect (inertia) of the hydrosystem  
407 cannot be assessed using the piezometric time series autocorrelograms the wells' piezometry  
408 is over-affected by other influences. Correlation of piezometry and EC with lake water levels is  
409 high for wells R5 and R6. Maximum lake - piezometry correlation in R5 is 0.6 for an offset of 0  
410 days (**Erreur ! Source du renvoi introuvable.**b) (fast pressure transfer). Lake level - EC  
411 correlation in R5 is not as high with a maximum of 0.13 for an offset ranging from 15 to 30 days:  
412 EC increases when the lake level increases. For the other wells (R1, R2 and R3), no correlation  
413 is observed between piezometry and lake level (diagrams not shown). Likewise, the EC of water  
414 pumped from these wells is not correlated with fluctuations in the La Ravière lake level.

415 Logically, the correlation between pumping rate and measured piezometry is negative  
416 (**Erreur ! Source du renvoi introuvable.**b) due, among other factors, to the large quadratic well  
417 head losses. The cross-correlogram between the pumping rate (QR5) and EC in R5 (**Erreur !**  
418 **Source du renvoi introuvable.**c) shows an inverse correlation.

#### 419 4.4.3. MULTIPLE INPUT SINGLE OUTPUT

420 The qualitative description of piezometric trends, water EC monitoring and cross-correlation  
421 analysis indicate that the variations linked to rainfall recharge are low-amplitude compared to  
422 other factors (La Ravière Lake levels for R5 and R6 and/or pumping rate). A multiple input  
423 single output (MISO) deconvolution analysis was therefore undertaken to highlight and better  
424 characterize the recharge mode.

425 *In this model (see the example for well R1 - **Erreur ! Source du renvoi introuvable.**), the aim was to reproduce the*  
426 *output (piezometry) from three inputs: (1) recharge, (2) R1 well discharge rate, and (3) aggregate discharge rate other*  
427 *than from well R1 ( $\Sigma Q = QB1 + QR2 + QR3$ ); QB1 being added in order to check the hypothesis that the B1 eastern*  
428 *compartment is the prolongation of the R4-R1 compartment. Calculation of piezometric impulse response was capped*  
429 *at a value of 256 days, corresponding to an approximate duration of recharge impulse response in pressure transfer*  
430 *(**Erreur ! Source du renvoi introuvable.**a). The model reproduces satisfactorily the piezometric trends observed at*  
431 *well R1 with a Nash criterion (Nash and Sutcliffe 1970) equal to 0.79 (**Erreur ! Source du renvoi introuvable.**a) with*  
432 *the relative contributions of the various components shown in **Erreur ! Source du renvoi introuvable.**c, d and e.*  
433 *Average contributions for R1 and those calculated for the other wells using the MISO method are summarized in*

434

435

436

437 Table 2. In R1, the variation linked to recharge reaches 4.6 m, compared to nearly 9.5 m for  
438 pumping in R1, and nearly 14.4 m for aggregate discharge ( $\Sigma Q$ ). Consequently, it is this last  
439 variable that mainly controls the long term changes in piezometry. The sensitivity analysis  
440 performed on QB1 demonstrates the hydraulic connection of the R4-R1 and HF4-B1  
441 compartments, and thus confirms the geophysical and geological interpretation.

442 On the basis of the MISO deconvolution results (Figures 8c, d and e), information related  
443 to the recharge process was extracted for each of the wells investigated. The cross-correlation  
444 analysis between rainfall and extracted recharge signal (water level (H) series deconvoluted  
445 from pumping effects using the MISO approach) is presented in **Erreur ! Source du renvoi**  
446 **introuvable.** The piezometric response to the recharge process is fast in the fissured horizon  
447 (Port well), with a maximum pressure transfer response of approximately 40-80 days after a  
448 recharge event (Figure 9a). The deep system's response to recharge is much longer for well B1  
449 (about 120 days) and wells R1 and R2 (around 100 days). The shape of the impulse response is  
450 indicative of pressure transfer within a weakly diffusive system that can be attributed to: (i) the

451 low permeability saprolite, (ii) the Nagesstratiformfissured zone, and (iii) the very low  
452 permeability of the underlying unfractured bedrock for the NMW wells. The response gap  
453 between B1 and R1/R2 (around 20 days) appears to be consistent considering the local  
454 geological structure: the B1 aquifer structure may be “confined” by the overlying impervious  
455 granite vein, and the water-bearing structure at the origin of the Rieumajou spring located  
456 between R1 and R2 may enhance the relationship between the deep fractures and the fissured  
457 horizon in surface. The responses of wells R3 and R5 are bimodal (**Erreur ! Source du renvoi**  
458 **introuvable**.b) with first a fast response and then a delayed response similar to the one  
459 observed on the other wells (B1, R1, R2) and a slightly faster response. The responses suggest  
460 that these wells are better connected (pressure transfer) to the subsurface formations.

461 The MISO approach was also used to describe mineralisation trends (EC) in water. It can  
462 be used to track the deep component of the system, as  $\text{HCO}_3$  content is linked to  $\text{CO}_2$  of deep  
463 origin. An example of a deconvolution result is given for well R1 (**Erreur ! Source du renvoi**  
464 **introuvable**.b). As described previously, three inputs were considered: (1) pumping time series  
465 for well R1 (QR1), (2) aggregate discharge rate at the other wells ( $\Sigma Q = \text{QB1} + \text{QR2} + \text{QR3}$ ), and  
466 (3) recharge time series corresponding to the recharge time series previously  
467 deconvoluted from piezometric data. Calculation of mineralisation impulse response was  
468 assumed at a maximum value of 512 days, as the duration of mass transfer is intuitively longer  
469 than that of pressure transfer (256 days). The mineralisation trend at borehole R1 is reproduced  
470 satisfactorily with the MISO approach (Figure 8b, Nash = 0.75). Increased pumping rates  
471 (compared to mean pumping rate) cause a decrease in mineralisation. Variations in pumping  
472 rates in R1 generate changes in mineralisation ( $\Delta$ ) in the range of  $-20 \mu\text{S}/\text{cm}$  at large temporal  
473 scale (Figure 8d). Increases in other pumping rates ( $\Sigma Q$ ) also result in decreased mineralisation  
474 (**Erreur ! Source du renvoi introuvable**.e). This cumulative pumping ( $\Sigma Q$ ) plays a significant  
475 role in mineralisation trends, which once again confirms that wells R1, R2, R3 and B1 are

476 hydraulically connected and, additionally, are connected to the same deep, CO<sub>2</sub>-rich water  
477 reservoir. Recharge induces an increase in mineralisation with a long-term cumulative  
478 effect(**Erreur ! Source du renvoi introuvable.**c): the succession of several wet cycles in 1994,  
479 1995 and 1996 (1668 mm, 1637 mm and 2412 mm rainfall, respectively) generates a greater  
480 mineralisation delta ( $\Delta = +60 \mu\text{S}/\text{cm}$ ) than dry cycles in 2001 (932 mm) and 2005 (1145 mm),  
481 ( $\Delta < +10 \mu\text{S}/\text{cm}$  a year). These results indicate that intensive recharge events do not result in a  
482 dilution of the mineral water by surface water. Instead, recharge events result in an increase in  
483 water mineralization because of increased pressure on the deeper parts of the system. This  
484 behaviour relative to recharge is similar to the one revealed for lake level increase.

#### 485 4.5. WATER-ROCK INTERACTION FROM HYDROCHEMISTRY AND ISOTOPE ANALYSIS

486 From the hydrogeochemical viewpoint (Table 3), the reservoir waters are characterised by  
487 a calcium bicarbonate facies (300 to 1200 mg/l of HCO<sub>3</sub>) typical of the “deep component” and by  
488 significant silica content (50 to 90 mg/l). The NMW therefore represents a fairly specific facies  
489 with typical basement water-rock interaction markers. The traditional indicators of high  
490 temperature water-rock interaction (Milot and Négrel, 2007) are low in concentration (low  
491 sodium content [ $< 7 \text{ mg/l}$ ], and very low lithium [ $< 0.1 \text{ mg/l}$ ] and boron [ $< 0.15 \text{ mg/l}$ ] contents). The  
492 NMW has a low chloride content (a few mg/l), this element being characteristic of the shallow  
493 component and mainly due to rainfall.

494 The carbon isotopic signature of  $\delta^{13}\text{C}$  from the gaseous CO<sub>2</sub> ( $\delta^{13}\text{C}$  ranges from  $- 5.6\text{‰}$  to  $-$   
495  $7.8\text{‰}$ ) clearly demonstrates its mantle origin according to Deines (1970) and Blavoux et al.  
496 (1982). In the  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  graph (**Erreur ! Source du renvoi introuvable.**), the water samples  
497 are located between the global meteoric water line (Craig 1961), which globally represents  
498 Atlantic origin rainfall, and the local meteoric water line determined for the Hérault  
499 region (Ladouche et al. 2009), affected by air masses from the Mediterranean. The graph does  
500 not highlight isotopic exchange phenomena, such as exchange with gaseous CO<sub>2</sub> or with rock

501 silicates at high temperature. The waters sampled in the shallow aquifer that were recharged at  
502 about 700 m a.s.l. are slightly more enriched in heavy isotopes compared to the NMW from the  
503 wells, which suggests recharge at a slightly higher elevation:  $800 \pm 50$  m a.s.l. with a  $-0.3 \text{ ‰}/100$   
504 m gradient (Ladouche et al. 2009), but that is nevertheless compatible with a local recharge. A  
505 paleoclimatic effect does not have to be factored in to explain the depleted  
506 isotopic signatures from wells B1 and HF4. Tritium data are explained as a result of mixing  
507 between old tritium-free water (deep sparkling water) and recent water (post 1952) with an  
508 exponential flow model (Malozewski and Zuber 1982), in which the distribution function of the  
509 transit time of water in the shallow aquifer is exponential. Tritium content in well F1 (1991) and in  
510 well R3 (1997 and 2010) may be explained by a mixture of 80% old water (prior to early 1950s)  
511 and 20% recent water, resulting in a mean transit time of more than 50 years.

512

513 The dominant aquifer lithology is Nages gneiss which is cross-cut by subvertical granite  
514 intrusions (**Erreur ! Source du renvoi introuvable.**). To conduct strontium isotope analysis,  
515 three rock samples from the Nages formation were selected from cores taken in well R6 and  
516 three granite samples from well R5 cores and a nearby outcrop of a granite vein (**Erreur !**  
517 **Source du renvoi introuvable.**). The results of water-rock interaction modelling for the granites  
518 and Nages gneiss (Table 4) show that, for the R6 sample (76 m depth), the absence of K-  
519 feldspar minerals in the model results in a  $^{87}\text{Sr}/^{86}\text{Sr}$  value of 0.71064 in the water at equilibrium,  
520 very close to the plagioclase value (0.710379). For the other R6 sample (96.9 m depth), the  
521 absence of plagioclase results in a higher computed value (0.71975) of the  $^{87}\text{Sr}/^{87}\text{Sr}$  ratio in the  
522 water at the equilibrium with the rock. The theoretical dissolution model was not applied to the R6  
523 sample (149.1 m depth—Cipolin marble) as the model is not applicable to carbonate rocks. The  
524 analyses were performed on the whole rock (Cipolin) as well as on the calcite that is present in  
525 light and dark layers. This Cipolin has the lowest Sr isotopic composition of all the rocks  
526 measured in the La Salvetat system. The isotopic composition of the calcite (0.708567), which

527 constitutes 69% of the light grey rock, has an isotopic signature that is fairly similar to that of the  
528 total rock. The residual calcite (calcite not yet dissolved) in dark beds is somewhat more  
529 radiogenic (0.709179).

530 The Srisotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) signature in water sampled from the wells ranges between  
531 0.708956 and 0.709121 (Table 3). Compared to theoretical values calculated above for waters in  
532 equilibrium with the various rock types, the results clearly show that pumped waters  
533 have Srisotope ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) signatures comparable to those measured in the Cipolin (R6, 149.1 m).  
534 The well waters are much less radiogenic than the waters calculated to be in equilibrium with the  
535 intrusive granites and spotted gneiss (R6, 96.9). The calcium bicarbonate facies of sparkling  
536 mineral waters is therefore acquired on contact with the Cipolins of the Nages formation.

## 537 5. NUMERICAL MODELLING

### 538 5.1. MODEL ARCHITECTURE

539 A model was developed for the South compartment exploited by wells R3, R2, R1, HF4 and  
540 B1. The compartment was modelled with two superimposed aquifer levels: a shallow reservoir  
541 and five deeper reservoirs, one for each production well (**Erreur ! Source du renvoi**  
542 **introuvable.**). The physical laws describing the various flows exchanged within this network of  
543 six reservoirs were selected on the basis of the conclusions of the multidisciplinary study. Thus,  
544 taking the piezometric data and location of the springs into account, it was ascertained that flow  
545 between the five reservoirs representing the deep aquifer is directed from the area around  
546 borehole HF4 towards the others (respectively towards the east (B1) and the west (F1, R2,  
547 R3...)) and reproduces the NMW discharge measured before exploitation began on the site.  
548 Horizontal flow generated by the head difference between the reservoirs is described in the  
549 model by a Darcy-type law. Vertical flow from the shallow reservoir towards the deep reservoirs  
550 is assumed proportional to the head difference in order to reproduce the leakage phenomenon

551 revealed by some hydraulic tests. Lastly, analysis has shown that, before the site was exploited,  
552 natural springs and shallow groundwater could be highly mineralised locally due to inflow of  
553 deep NMW into the shallow aquifers. To reproduce this mineralization, the deep reservoirs were  
554 forced to empty into the shallow reservoir according to a decreasing exponential (emptying time  
555 5 to 10 days depending on the reservoir) which terminates below a certain piezometric threshold.

556 A "soil" module in the model calculates the partitioning of rainwater into evapotranspiration,  
557 runoff, and infiltration according to the Thornthwaite classical model. Runoff flows towards the La  
558 Raviège Lake outside the modelled system. Infiltration comprises two components, with given  
559 chemical composition. The first component has a "shallow" type geochemical signature and is  
560 imposed as input to the shallow reservoir. The chemical composition of water is not calculated by  
561 the model but rather is a boundary condition, constant over time. In order to reproduce the  
562 observed inflow of NMW in the shallow aquifer (reservoir), this boundary condition was spatialized.  
563 Consequently, the chemical composition of water in the shallow reservoir could vary from one  
564 reservoir to the other. Thus, a composition C1 (Figure 11) is imposed for transfers from the  
565 shallow reservoir feeding R1, R2 and R3 reservoirs, and a more mineralised composition C2 is  
566 imposed as input for feeding B1 and HF4. This conceptualization allows for reproduction of a  
567 higher chemical inertia of B1 and HF4 wells as compared to R1, R2 and R3. The second  
568 component feeding the deep reservoirs is the deep geochemical signature C3. All these imposed  
569 compositions are chosen among available results of surface or deep water analyses. These two  
570 components are imposed at the reservoir input with a time lag relative to the rainfall that  
571 generated them. This is used to introduce inertia into the model on the basis of a maximum lag  
572 of 80 to 130 days as highlighted by time series analysis.

573 The chemical composition of the water in each of the five reservoirs is calculated by the  
574 model according to a mixing process due to flow exchange between the reservoirs. Water-rock  
575 geochemical reactions are also taken into account where necessary. The chemical  
576 heterogeneous reactions that produce or consume calcium, carbon and silica in aqueous phase

577 are described by first-order kinetic laws. The other chemical elements are considered non-  
578 reactive.

579         The model was numerically transposed using Matlab and Simulink© software with a one-  
580 day time step. The physical parameters of the model were determined according to the results of  
581 the multidisciplinary study. In this way, the dimensions of the five deep reservoirs are such that  
582 they form a deeply-rooted, lens-shaped structure 50 m wide and 600 m long. As defined by the  
583 model, these reservoirs are unconfined. An effective porosity of 1%, a classical value in the  
584 shallow weathered-fractured zone of crystalline rocks (Marechal et al. 2006; Maréchal et al.  
585 2004), leads, at an equivalent water head, to a body of water of the same order of magnitude as  
586 that stored in the natural confined aquifer (storage coefficient estimated at  $5 \times 10^{-4}$ ) including wells  
587 R3, R2, R1, HF4 and B1. The reservoir time constants are fitted so that, without pumping, flow is  
588 within an order of magnitude of the estimated discharge of natural springs before  
589 production, mainly to the west (R3) and to a much lower extent to the east (B1). In order to  
590 estimate the other model parameters, time series of production discharge, daily piezometric data  
591 and weekly chemical analyses are available on a 10 to 22 years period. A long transient period  
592 was needed for initialization because, owing to the inertia of the hydrogeological system, the  
593 observed system is never in a stationary regime. The area of the upper reservoir's catchment  
594 zone was determined during fitting, at  $0.6 \text{ km}^2$ . This value is in agreement with the  $^{18}\text{O}$  data and  
595 the physical geography of the site, and corresponds to 3/4 of the surface catchment area. Lastly,  
596 to most accurately reflect the concentrations of chemical species observed in the water from the  
597 different wells, the chemical reactivity of calcium, carbon and silica were considered. For the  
598 other chemical elements considered by the model, the perfect tracer hypothesis is acceptable  
599 (i.e. the chemical species are considered un-reactive).

## 600         5.2. SIMULATION

601 The calculated water levels were compared to the piezometric levels measured  
602 (corrected for quadratic head loss) over the calibration period (1991-2012) after initialisation. The  
603 results obtained at wells R1 and R2, which benefit from the longest observation period, are given  
604 for illustration purposes in **Erreur ! Source du renvoi introuvable.** The high amplitude  
605 fluctuations observed (and simulated) over the period 1994-1998 are linked to high precipitation  
606 periods. The year 1996 is an atypical year with 2,412 mm of precipitation, while the annual mean  
607 is 1,370 mm over the period 1987-2011. The model also reproduces satisfactorily long-term  
608 concentration dynamics (**Erreur ! Source du renvoi introuvable.**). The annual fluctuations are  
609 consistent with the observations. In particular, the model correctly forecasts increased  
610 concentrations following a series of rainy years (**Erreur ! Source du renvoi introuvable.**).  
611 However, in the short-term, the model lacks inertia and does not sufficiently absorb fluctuations  
612 compared to reality.

613 Once fitted, the numerical model was used to explore how the system functions and to  
614 verify the consistency of the conceptual model with the entire set of observations. For instance,  
615 in its natural state (without pumping), the discharge from the reservoirs approximates 60 m<sup>3</sup>/day  
616 for R1 and R2, and 10 m<sup>3</sup>/day for B1. These values match the estimated discharge from natural  
617 springs before exploitation in each area. In its natural state, the shallow reservoir mainly feeds  
618 the deep reservoir HF4 (which receives 45% of flow from the shallow reservoir), followed by R1  
619 and R2 (20% each). These flow differences induce pressure differentials between the deep  
620 reservoirs, which induce flow from HF4 towards B1 (to the east) and from HF4 to R1 (to the  
621 west), and from R2 towards R3. Modelling therefore allows one to rule out that sector B1-HF4  
622 may not be hydraulically connected to the western part of the aquifer. From the geochemical  
623 standpoint, 50% of flow feeding reservoirs B1 and R1 correspond to highly mineralised water  
624 (deep geochemical signature), versus 30% in HF4 and R2.

## 625 6. DISCUSSION

626 The absence of connectivity between the North and South compartments (piezometry,  
627 interference between wells), and their contrasting hydrodynamic functioning demonstrate the  
628 existence of two permeable bodies oriented E-W (N100-110°E) (**Erreur ! Source du renvoi**  
629 **introuvable.**a and b). This orientation is consistent with the major extensional structures related  
630 to the alpine orogeny, which resulted from the Miocene opening of the western Mediterranean.  
631 Furthermore, signal treatment and modelling demonstrated the continuity of the southern  
632 compartment towards the East until at least B1 well. These hydraulic data agree with the  
633 geological structure deduced from the geophysics and calibrated against the geological data  
634 from the wells and the basic data such as topography, location of NMW springs, and piezometry.  
635 The geology alone, however, was not clear enough to be demonstrative. Based on these findings,  
636 it appears that the granite veins do not explain the permeability of the La Salvetat mineral  
637 aquifer. Water mineralisation is primarily acquired at depth on contact with the Cipolin  
638 marbles which must, consequently, be deeply rooted, while the granites form fairly thin local veins,  
639 which are not deeply rooted. Analysis of pumping and interference tests between production  
640 wells, in addition to the structure (two distinct permeable bodies) and the characterization of their  
641 hydrodynamic parameters, highlights the existence of three major hydraulic boundary conditions.

642 First, the presence of a leakage effect for several wells, correlated with the existence of a  
643 discontinuous aquifer in the stratiform fissured layer, shows that it is drained *per descensum* by  
644 leakage into the deep fractures intersected by the wells. In this type of crystalline rock, this  
645 aquifer corresponds to the middle part of the weathering profile formed by a fissured layer in the  
646 Nages gneiss, itself supplied through leakage from overlying weathered products (saprolite). The  
647 relationship between the deep aquifer tapped by the wells and this aquifer is confirmed by the  
648 hydrochemistry and, above all, by the numerical model, which requires this type of vertical  
649 exchange to correctly reproduce piezometric trends and the water chemical composition.

650 Second, no-flow boundary conditions show that the deep fractures drain a spatially closed  
651 aquifer with a width (North-South) of about 50 to 200 m (pumping tests, geophysics) and a

652 length of about 600 meters (West to East, from R4 at least to B1) which is realistic considering the  
653 pumping test and modelling data. Well data (discrete water bearing structures separated by  
654 impermeable formations) show that within this subvertical fractured strip, only a small part of the  
655 volume (about one percent in volume) is fractured and permeable.

656 Third, the partial penetration of the wells is confirmed by modelling which requires at least a  
657 depth of 600 meters for each reservoir to account for the high inertia of the mineral system, most  
658 of the pumped water flowing upward from this great depth. This suggests that each permeable  
659 structure is very deeply rooted with a fissured zone along main faults. Both these two faults  
660 appear to be tension joints. Data currently available do not provide a basis for determining  
661 whether other joints exist further North or South. In addition, the available geophysics does not  
662 suggest it. Nevertheless, new drillings are scheduled at the eastern tip of the southern structure  
663 (East of B1) in order to check its potential eastern continuation.

664 Another similar structure in the Nages gneiss gives rise to a mineral spring (Font Rouge), 6  
665 km west of the investigation site with a similar hydrochemical composition. It is the only such  
666 spring within a radius of about 50 km around La Salvetat. Thus, such permeable structures are  
667 not common. They cannot be identified only by simple means (lineament analysis, for instance).  
668 Such fractures are mostly revealed by NMW outflow where they cross-cut a topographical low.  
669 Other similar fractures not cross-cutting a topographical low probably exist, but they are not  
670 identifiable at the surface by a NMW spring.

671 Signal processing on piezometric and geochemical data logically shows the existence of  
672 two types of groundwater flow: (i) a "fast" recharge corresponding to local flow path (40-80  
673 days), within the non-mineralized shallow aquifer of the fissured layer, and (ii) the increase of the  
674 NMW component hydraulic head (80-130 days) itself resulting in an increase in mineralisation.  
675 High water levels in the shallow aquifer (related to rainfall or to lake level variations) give rise to  
676 an increase in the mineral component. The inertia of the system is such that several successive  
677 wet years induce a continuous increase in this mineral component. Modelling also shows that R3

678 (and particularly R4) is apparently not directly supplied by the deep permeable structure, but  
679 results from mixing between overflow from mineral water coming from the East (B1, HF4, R1,  
680 R2) and ancient waters (without tritium) from the shallow fissured aquifer. Additional modelling of  
681 the northern compartment (R6, R5, HF2) scheduled for the second phase of the project will  
682 undoubtedly fine-tune this conceptual model, particularly the possible relationships between the  
683 two systems through the fissured layer, and the recharge evaluation.

684 This investigation showed the importance of characterising initial flow conditions (and  
685 geochemistry) before the system went into production in order to understand how these  
686 hydrothermal systems function. In fact, these elements were essential for reliably fitting the  
687 hydrodynamic model. Such a characterization should systematically be performed in detail prior  
688 to beginning to pump in a NMW system. The study also illustrates the need for suitable analytical  
689 models for modelling pumping tests where it is necessary to consider, among other parameters,  
690 the anisotropy in hydraulic conductivity of a faulted zone, and the partial penetration of wells  
691 within such a faulted aquifer. This could be particularly helpful for better characterization of the  
692 B1 compartment to improve the system geometry, and also to better constrain the depth of the  
693 fracture or, at least, if it is very deep, to assess it. In fact, it is probable that at B1 the far no-flow  
694 boundaries appear very late after the start of the pumping because of such a very strong  
695 anisotropy of the pumped fractured zone, and also as a consequence of the very deep root of  
696 the fractured zone.

## 697 7. CONCLUSION

698 A detailed characterization of a complex NMW system at La Salvetat (France) was made  
699 possible through the use of a combination of techniques. Two neighbouring fractured zones in the  
700 Nages gneiss constitute the main pathways for deep CO<sub>2</sub> and NMW to rise to the land's surface.  
701 Geological investigations, pumping test analysis, time series signal processing,  
702 hydrogeochemical and isotopes approaches, and numerical modelling provided complementary

703 information on the geometry and hydrodynamic characteristics of the permeable structure, and  
704 on the functioning of this mineral system. This applied research investigation demonstrates the  
705 need of multidisciplinary approaches and modelling (quantity, quality) as a tool for understanding  
706 complex NMW systems. Only through a combination of evidences, each obtained from one  
707 discipline, which on its own did not lend sufficient insight, was it possible to build a representative  
708 conceptual model. This model then allowed determining, with an acceptable degree of certainty,  
709 the geometry of the permeable structure at the origin of the mineral system, whereas most  
710 classical studies, mainly based only on a structural geology approach, do not generally exhibit  
711 this degree of reliability and are merely speculative. The multidisciplinary approach also allowed  
712 a more thorough understanding of the hydrodynamic and hydrogeochemical functioning of the  
713 system, from a rather great depth (a few hundred meters) to the surface. This knowledge about  
714 the structure and functioning of such a sparkling NMW system is of interest as it may provide a  
715 conceptual model that could be used at other NMW sites. The knowledge of the system is also of  
716 high interest for the bottling company that is already applying it for the sustainable management  
717 of the spring, to program additional hydrogeological surveys aimed at increasing the available  
718 resource, and to implement protection policies on its watershed. It also opens up perspectives for  
719 a complete spatialized deterministic 3-D modelling of such complex hydrosystems.

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## 724 9. REFERENCES

725 Battani A, Sarda P, Prinzhofer A (2000) Basin scale natural gas source, migration and trapping traced by  
726 noble gases and major elements: the Pakistan Indus basin. *Earth and Planetary Science Letters*  
727 181: 229-249 doi: 10.1016/S0012-821X(00)00188-6

728 Black JH (1994) Hydrogeology of fractured rocks - a question of uncertainty about geometry. Applied  
729 Hydrogeology 2: 56-70 doi: 10.1007/s100400050049

730 Blavoux B, Dazy J (1990) Characterization of a CO<sub>2</sub> province in the Southeastern basin of France.  
731 Hydrogéologie 4: 241-252

732 Bullen TD, White AF, Blum AE, Harden JW, Schulz MS (1997) Chemical weathering of a soil  
733 chronosequence on granitoid alluvium; II, Mineralogic and isotopic constraints on the behavior  
734 of strontium. *Geochimica et Cosmochimica Acta* 61: 291-306 doi: 10.1016/S0016-  
735 7037(96)00344-4

736 Clemente WC, Villadolid-Abrigo FL (1993) The Bulalo geothermal field, Philippines: reservoir  
737 characteristics and response to production. *Geothermics* 22: 381-394 doi: 10.1016/0375-  
738 6505(93)90026-J

739 Collon P, Fabriol R, Vaute L, Pinault JL, Bues M (2002) Modelling changes in sulphate concentration in  
740 discharge water from the abandoned iron mine of SaizeraisSWEMP 2002 - International  
741 Symposium on Environmental issues and Waste Management in Energy and Mineral Production  
742 7th edn, Cagliari.

743 Craig H (1961) Isotopic Variations in Meteoric Waters. *Science* 133: 1702-1703 doi:  
744 10.1126/science.133.3465.1702

745 Demange M, Guérangé-Lozes J, Guérangé B (1995) Carte géol. France (1/50 000) feuille Lacaune  
746 (Geological map of France - sheet Lacaune) BRGM, Orléans, pp. Notice explicative par M.  
747 Demange, J. Guérangé-Lozes, B. Guérangé et coll. .

748 Dewandel B, Lachassagne P, Wyns R, Marechal JC, Krishnamurthy NS (2006) A generalized 3-D geological  
749 and hydrogeological conceptual model of granite aquifers controlled by single or multiphase  
750 weathering. *Journal of Hydrology* 330: 260-284 doi: 10.1016/j.jhydrol.2006.03.026

751 Dewandel B, Lachassagne P, Zaidi FK, Chandra S (2011) A conceptual hydrodynamic model of a geological  
752 discontinuity in hard rock aquifers: Example of a quartz reef in granitic terrain in South India.  
753 *Journal of Hydrology* 405: 474-487 doi: 10.1016/j.jhydrol.2011.05.050

754 Ehlig-Economides C (1988) Use of the pressure derivative for diagnosing pressure-transient behavior. *J.*  
755 *Pet. Technol*: 1280–1282 doi: 10.2118/18594-PA

756 Gustafson G, Gylling B, Selroos J-O (2009) The Aespoe Task Force on groundwater flow and transport of  
757 solutes: bridging the gap between site characterization and performance assessment for  
758 radioactive waste disposal in fractured rocks. *Hydrogeology Journal* 17: 1031-1033 doi:  
759 10.1007/s10040-008-0419-6

760 Hantush MS (1960) Aquifer tests on partially penetrating wells. *Journal of Geophysical Research* 65:  
761 2495-2495

762 Kerrick DM, Caldeira K (1998) Metamorphic CO<sub>2</sub> degassing from orogenic belts. *Chemical Geology* 145:  
763 213-232 doi: 10.1016/S0009-2541(97)00144-7

764 Kothyari UC, Singh VP (1999) A multiple-input single-output model for flow forecasting. *Journal of*  
765 *Hydrology* 220: 12-26 doi: 10.1016/S0022-1694(99)00055-4

766 Lachassagne P, Maréchal J, Sanjuan B (2009) Hydrogeological model of a high-energy geothermal field  
767 (Bouillante area, Guadeloupe, French West Indies). *Hydrogeology Journal* 17: 1589-1606 doi:  
768 10.1007/s10040-009-0486-3

769 Lachassagne P, Wyns R, Dewandel B, Lachassagne P, Wyns R, Dewandel B, P. L, et al. (2011) The fracture  
770 permeability of Hard Rock Aquifers is due neither to tectonics, nor to unloading, but to  
771 weathering processes. *Terra Nova* 23: 145-161 doi: 10.1111/j.1365-3121.2011.00998.x

772 Ladouche B, Aquilina L, Dörfliger N (2009) Chemical and isotopic investigation of rainwater in Southern  
773 France (1996-2002): Potential use as input signal for karst functioning investigation. *Journal of*  
774 *Hydrology* 367: 15-15 doi: 10.1016/j.jhydrol.2009.01.012

775 Mangin A (1984) The Use of Autocorrelation and Spectral Analyses to Obtain a Better Understanding of  
 776 Hydrological Systems (Pour une Meilleure Connaissance des Systemes Hydrologiques a Partir des  
 777 Analyses Corelatoire et Spectrale). Journal of Hydrology 67: 25-43  
 778 Marechal JC, Dewandel B, Ahmed S, Galeazzi L, Zaidi FK (2006) Combined estimation of specific yield and  
 779 natural recharge in a semi-arid groundwater basin with irrigated agriculture. Journal of  
 780 Hydrology 329: 281-293 doi: 10.1016/j.jhydrol.2006.02.022  
 781 Maréchal JC, Dewandel B, Subrahmanyam K (2004) Use of hydraulic tests at different scales to  
 782 characterize fracture network properties in the weathered-fractured layer of a hard rock aquifer.  
 783 Water Resources Research 40 doi: 10.1029/2004wr003137  
 784 Morosini M, Rhen I (2000) Hydrogeological characterization of fractured rock for Sweden's nuclear waste  
 785 storage. Proceedings of the ... IAH Congress on Groundwater... 30: 785-789  
 786 Nash JE, Sutcliffe JV (1970) River flow forecasting through conceptual models part I — A discussion of  
 787 principles. Journal of Hydrology 10: 282-290 doi: [http://dx.doi.org/10.1016/0022-](http://dx.doi.org/10.1016/0022-1694(70)90255-6)  
 788 [1694\(70\)90255-6](http://dx.doi.org/10.1016/0022-1694(70)90255-6)  
 789 Negrel P, Casanova J, Aranyossy J-F (2001) Strontium isotope systematics used to decipher the origin of  
 790 groundwaters sampled from granitoids; the Vienne case (France). Chemical Geology 177: 287-  
 791 308 doi: 10.1016/S0009-2541(00)00414-9  
 792 Nind T (1965) Influences of absolute and partial hydrologic barriers on pump test results. Canadian  
 793 Journal of Earth Sciences 2: 309-323 doi: doi:10.1139/e65-025  
 794 Petelet Giraud E, Negrel P, Casanova J (2003) Variability of Sr-87/Sr-86 in water draining granite revealed  
 795 after a double correction for atmospheric and anthropogenic inputs. HYDROLOGICAL SCIENCES  
 796 JOURNAL JOURNAL DES SCIENCES HYDROLOGIQUES 48: 729-742  
 797 Pin C, Bassin C (1992) Evaluation of a strontium specific extraction chromatographic method for isotopic  
 798 analysis in geological materials. Analytica Chimica Acta 269: 249-255 doi: 10.1016/0003-  
 799 2670(92)85409-Y  
 800 Pinault J-L, Plagnes V, Aquilina L, Bakalowicz M (2001) Inverse modeling of the hydrological and the  
 801 hydrochemical behavior of hydrosystems: Characterization of karst system functioning. Water  
 802 Resources Research 37: 2191-2204 doi: 10.1029/2001WR900018  
 803 Renard P, Glenz D, Mejias M (2009) Understanding diagnostic plots for well-test interpretation.  
 804 Hydrogeology Journal 17: 589-600 doi: 10.1007/s10040-008-0392-0  
 805 Shipton ZK, Evans JP, Dockerill B, Heath J, Williams A, Kirchner D, Kolesar PT (2005) Natural leaking CO<sub>2</sub>-  
 806 charged systems as analogs for failed geologic storage reservoirs. In: Benson SM (ed) Carbon  
 807 dioxide capture for storage in deep geological formations:699–712.

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809 **Tables**

810 Table 1: Summary of pumping test results

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| PW | Geol | No. of Tests | OW          | Diagnostic feature      | Analytical model            | T or T1 (m <sup>2</sup> /s) | S                      | Distance to boundary (m) | T2 (m <sup>2</sup> /s) |
|----|------|--------------|-------------|-------------------------|-----------------------------|-----------------------------|------------------------|--------------------------|------------------------|
| R1 | N    | 3            | R2, DAC, P1 | Partitioned aquifer, PP | Hantush (1961); Nind (1965) | 2.3 x 10 <sup>-4</sup>      | 5.1 x 10 <sup>-4</sup> | 180                      | 4.5 x 10 <sup>-4</sup> |
| R2 | N    | 2            | R1, DAC,    | Partitioned aquifer     | Nind (1965)                 | 2.3 x 10 <sup>-4</sup>      | 5.2 x 10 <sup>-4</sup> | 180                      | 4.7 x 10 <sup>-4</sup> |

| P1  |   |    |               |                              |   |                      |                      |                    |                      |
|-----|---|----|---------------|------------------------------|---|----------------------|----------------------|--------------------|----------------------|
| R3  | N | 2  | R1, R2        | Partitioned aquifer          | Nind (1965)                               | $2.4 \times 10^{-4}$ | $5.7 \times 10^{-4}$ | 300                | $2.6 \times 10^{-5}$ |
| R4  | N | 3  | MLC2, ML3, P3 | Bounded aquifer with leakage | 4 orthogonal no-flow boundaries + leakage | $5.4 \times 10^{-4}$ | $5.0 \times 10^{-4}$ | 100, 100, 140, 260 | -                    |
| R5  | G | 2  | R6*           | Partitioned aquifer (PP)     | Hantush (1961); Nind (1965)               | $5.0 \times 10^{-4}$ | $4.0 \times 10^{-5}$ | Not evaluated      | -                    |
| R6  | N | 10 | R5*           | Partitioned aquifer          | Nind (1965)                               | $1.8 \times 10^{-4}$ | $1.3 \times 10^{-5}$ | 450                | $9.3 \times 10^{-4}$ |
| DAC | N | 1  | R1, R2        | Homogeneous aquifer          | Theis (1935)                              | $1.4 \times 10^{-4}$ | $3.9 \times 10^{-4}$ | -                  | -                    |
| P3  | N | 1  | R3, R4        | Bounded aquifer              | 4 orthogonal no-flow boundaries           | $5.0 \times 10^{-4}$ | $8.3 \times 10^{-4}$ | 70, 70, 70, 70     | -                    |
| B1  | N | 4  | -             | Channelized flow             | 2 parallel no-flow boundaries             | $9.0 \times 10^{-5}$ | -                    | 400, 400           | -                    |
| HF4 | N | 2  | B1            | Channelized flow             | 2 parallel no-flow boundaries             | $8.7 \times 10^{-3}$ | $4.0 \times 10^{-4}$ | 30, 30             | -                    |

812 PW pumping well; OW observation well; T – transmissivity (in case of partitioned aquifer: T1 - transmissivity of the  
813 local aquifer where the PW is drilled and T2 – transmissivity of the aquifer beyond the boundary); S – storativity.  
814 Geology: N – Nages and G – granite; PP: Partial penetration;\*no reaction of other wells

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819 Table 2: Relative contributions of hydrological time series to the water level in five production wells

| Mean Relative Contributions |                             |                                     |  |   |  |
|-----------------------------|-----------------------------|-------------------------------------|--|---|--|
| Well                        | Depth of well screening (m) | Recharge (%)<br>[maximum amplitude] | Discharge at the well (%)<br>[maximum amplitude] | Discharge of the other wells (%)<br>[maximum amplitude] | Ravière Lake level(%)<br>[maximum amplitude] |
| R1                          | 60-87                       | 13%<br>[4.6 m]                      | 37%<br>[9.5 m]                                   | 50%<br>[14.4 m]   | No contribution                              |
| B1                          | 111-121                     | 39%<br>[3.1 m]                      | 61%<br>[4.9 m]                                   | -   | No contribution                              |
| R2                          | 45-101                      | 12%<br>[2.2 m]                      | 44%<br>[5 m]                                     | 54%<br>[8.4 m]  | No contribution                              |
| R3                          | 41.9-44                     | 8%<br>[1.8 m]                       | 87%<br>[5.5 m]                                   | 5%<br>[1.6 m]   | No contribution                              |
| R5                          | 73-130                      | 8%<br>[1 m]                         | 42%<br>[6 m]                                     | -   | 50%<br>[7 m]                                 |

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Table 3 : Major cations and anions (Na, K, Mg, Ca, Cl, HCO<sub>3</sub>, SO<sub>4</sub>, and SiO<sub>2</sub> in mg/L), trace elements (Li, B, Sr, Fe, Mn and Ba in µg/L), stable isotopes of the water molecule (δ<sup>2</sup>H and δ<sup>18</sup>O), tritium, stable isotopes (δ<sup>13</sup>C) of the dissolved CO<sub>2</sub> and <sup>87</sup>Sr/<sup>86</sup>Sr ratios

| Well   |                 | B1       | R5       | R3       | R6       | R1       | R2       | HF4      |
|--|-----------------|----------|----------|----------|----------|----------|----------|----------|
|  | Date (dd/mm/yy) | 10/09/10 | 10/09/10 | 10/09/10 | 10/09/10 | 10/09/10 | 10/09/10 | 14/09/11 |
| pH   |                 | 5.8      | 6.2      | 6.4      | 6.2      | 6.1      | 5.9      | 5.81     |
| EC   | µS/cm           | 1645     | 884      | 477      | 588      | 1076     | 816      | 1460     |
| Temp   | °C              | 14.7     | 14.0     | 15.1     | 14.1     | 14.0     | 14.3     | 13.0     |
| SiO <sub>2</sub>                             | mg/l            | 81.0     | 91.3     | 61.5     | 80.4     | 74.9     | 71.5     | 96.8     |
| Na <sup>+</sup>                              | mg/l            | 6.6      | 4.8      | 4.5      | 3.4      | 5.3      | 4.4      | 7.1      |
| K <sup>+</sup>                               | mg/l            | 2.9      | 2.0      | 2.3      | 1.5      | 2.4      | 2.3      | 2.9      |
| Ca <sup>2+</sup>                             | mg/l            | 374      | 176      | 137      | 112      | 222      | 162      | 373      |
| Mg <sup>2+</sup>                             | mg/l            | 15.6     | 9.5      | 7.0      | 4.8      | 10.5     | 7.5      | 15.4     |
| Cl <sup>-</sup>                              | mg/l            | 3.7      | 4.2      | 4.1      | 4.2      | 4.5      | 5.1      | 3.4      |
| HCO <sub>3</sub> <sup>-</sup>                | mg/l            | 1186     | 561      | 289      | 358      | 681      | 544      | 1192     |
| SO <sub>4</sub> <sup>2-</sup>                | mg/l            | 9.0      | 20.3     | 9.0      | 7.4      | 43.6     | 7.9      | 8.5      |
| NO <sub>3</sub> <sup>-</sup>                 | mg/l            | <0.5     | <0.5     | <0.5     | <0.5     | <0.5     | <0.5     | <0.5     |
| NH <sub>4</sub> <sup>+</sup>                 | mg/l            | 0.14     | 0.07     | <0.05    | <0.05    | 0.05     | 0.19     |          |
| F <sup>-</sup>                               | mg/l            | 0.3      | 0.4      | 0.3      | 0.4      | 0.3      | 0.4      | 0.3      |
| Fe(tot)                                      | µg/l            | 14500    | 8430     | 5230     | 5790     | 11400    | 7660     | 48024    |
| Mn(tot)                                      | µg/l            | 1581     | 581      | 458      | 455      | 843      | 568      | 1722     |
| Ba   | µg/l            | 12.47    | 11.35    | 7.58     | 8.19     | 7.33     | 7.27     | 50.1     |
| B <sup>-</sup>                               | µg/l            | 59.4     | 24       | 32.1     | 16.2     | 36.1     | 39.6     | 10.4     |
| Li <sup>+</sup>                              | µg/l            | 28.3     | 21.5     | 16.9     | 13.1     | 21.2     | 16.9     | 21.9     |
| Sr <sup>2+</sup>                             | µg/l            | 1910     | 914      | 780      | 601      | 1210     | 868      | 1718     |
| <sup>87</sup> Sr/ <sup>86</sup> Sr           |                 | 0.708985 | 0.709048 | 0.709121 | 0.708963 | 0.709018 | 0.709024 | 0.708956 |
| 2σ for <sup>87</sup> Sr/ <sup>86</sup> Sr(m) |                 | 0.000008 | 0.000008 | 0.000009 | 0.000008 | 0.000007 | 0.000008 | 0.000009 |
| δD   | ‰               | -46.0    | -44.5    | -45.3    | -45.3    | -45.2    | -45.1    | -48      |
| δ <sup>18</sup> O                            | ‰               | -7.3     | -7.1     | -7.2     | -7.1     | -7.2     | -7.2     | -7.5     |
| <sup>3</sup> H                               | UT              | 2        | 2        | <1       | 2        | 3        | 2        | 3        |

|                                       |   |      |      |      |      |      |      |   |
|---------------------------------------|---|------|------|------|------|------|------|---|
| 2σ for <sup>3</sup> H(m)              |   | 1    | 1    |      | 1    | 1    | 1    | 1 |
| d <sup>13</sup> C (CO <sub>2g</sub> ) | ‰ | -5.6 | -6.7 | -7.8 | -7.8 | -6.6 | -6.4 |   |

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833 Table 3(continued)

|   |       | P3       | MLC1     | R4       | HF1      | HF2      | HF3      | HF5      |
|---|-------|----------|----------|----------|----------|----------|----------|----------|
|   |       | 08/09/10 | 08/09/10 | 13/09/10 | 13/12/11 | 27/12/11 | 15/09/11 | 13/12/11 |
| pH  |       | 6.77     | 6.89     | 6.64     | 7.20     | 6.50     | 7.23     | 7.80     |
| EC  | μS/cm | 232      | 132      | 718      | 126      | 863      |          | 179      |
| Temp  | °C    |          |          |          | 14.0     |          | 11.7     | 14.0     |
| SiO <sub>2</sub>                              | mg/l  | 10.4     | 13.9     | 35.6     | 19.5     | 39.0     | 15.4     | 10.2     |
| Na <sup>+</sup>                               | mg/l  | 4.7      | 3.8      | 4.7      | 4.9      | 8.7      | 3.7      | 3.4      |
| K <sup>+</sup>                                | mg/l  | 1.0      | 1.0      | 1.7      | 2.8      | 2.5      | 0.8      | 1.5      |
| Ca <sup>2+</sup>                              | mg/l  | 40       | 22       | 182      | 38       | 203      | 26       | 30       |
| Mg <sup>2+</sup>                              | mg/l  | 2.4      | 1.5      | 6.7      | 3.2      | 11.6     | 1.5      | 2.5      |
| Cl <sup>-</sup>                               | mg/l  | 18.5     | 7.5      | 7.9      | 3.0      | 3.0      | 4.0      | 6.5      |
| HCO <sub>3</sub> <sup>-</sup>                 | mg/l  | 107      | 76       | 542      | 79       | 686      | 82       | 106      |
| SO <sub>4</sub> <sup>2-</sup>                 | mg/l  | 3.5      | 3.0      | 9.5      | 5.5      | 5.5      | 2.0      | 2.5      |
| NO <sub>3</sub> <sup>-</sup>                  | mg/l  | 14.5     | 1.6      | 0.4      | 0.40     | 3.6      | 1.6      | 5.30     |
| NH <sub>4</sub> <sup>+</sup>                  | mg/l  |          |          |          |          | <0.02    |          |          |
| F <sup>-</sup>                                | mg/l  |          |          |          | <0.1     |          | <0.1     | <0.1     |
| Fe(tot)                                       | μg/l  | 1.5      | 4        | 194      |          | 0.60     | 24       |          |
| Mn(tot)                                       | μg/l  | 0.3      | 0.5      | 180      | 374      | 0.10     | 13.5     | 18       |
| Ba  | μg/l  | 7        | 7.5      | 14       | 12.5     | 17       | 4.1      | 6.5      |
| B-  | μg/l  | <20      | 30       | <20      | <20      |          | 3.0      | <20      |
| Li <sup>+</sup>                               | μg/l  | 1.5      | 1.5      | 21.0     | 5.5      | 29.0     | 1.7      | 3.5      |
| Sr <sup>2+</sup>                              | μg/l  | 301      | 157      | 1201     | 397      | 1370     | 307      | 286      |
| <sup>87</sup> Sr/ <sup>86</sup> Sr            |       | 0.708933 | 0.709473 | 0.708840 |          |          | 0.709012 |          |
| 2σ for <sup>87</sup> Sr/ <sup>86</sup> Sr (m) |       | 0.000009 | 0.000009 | 0.000009 |          |          | 0.000009 |          |
| δD  | ‰     | -45.2    | -42.9    | -44.5    |          |          | -46.5    |          |
| δ <sup>18</sup> O                             | ‰     | -7.2     | -6.9     | -7.0     |          |          | -7.2     |          |
| <sup>3</sup> H                                | UT    | 3        | 3        | 2        |          |          |          |          |
| 2σ for <sup>3</sup> H(m)                      |       | 1        | 1        | 1        |          |          |          |          |

834  $\sigma$ : standard deviation

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838 Table 4: Strontium (Sr) and rubidium (Rb) data on rock samples

| Formation           | Sample (depth)      | Mineral | Rb (ppm) | Rb* (ppm) | Sr (ppm) | Sr* (ppm) | $^{87}\text{Sr}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr}$ W-model |
|---------------------|---------------------|---------|----------|-----------|----------|-----------|---------------------------------|---|
|                     |                     |         |          |           |          |           |                                 |   |
| Granite             | Granite 8 (outcrop) | TR      | 271      | -         | 76       | -         | 0.755219                        | 0.76116                                 |
|                     |                     | P+Q     | 135      | 271       | 46       | 92        | 0.748866                        |   |
|                     |                     | K-F     | 532      | -         | 104      | -         | 0.773991                        |   |
|                     |                     | B       | 609      | -         | 10       | -         | 1.390815                        |   |
| Granite             | R5 (102.8 m)        | TR      | 373      | -         | 48       | -         | 0.799635                        | 0.80615                                 |
|                     |                     | P+Q     | 219      | 547       | 34       | 84        | 0.784069                        |   |
|                     |                     | K-F     | 530      | -         | 76       | -         | 0.793338                        |   |
|                     |                     | B       | 1807     | -         | 10       | -         | 2.805149                        |   |
| Granite (pegmatite) | R5 (117.4 m)        | TR      | 451      | -         | 28       | -         | 0.897886                        | 0.88075                                 |
|                     |                     | P+Q     | 273      | 414       | 20       | 30        | 0.872317                        |   |
|                     |                     | K-F     | 959      | -         | 45       | -         | 0.959064                        |   |
| Nages gneiss        | R6 (76 m)           | TR      | 94       | -         | 471      | -         | 0.712446                        | 0.71064                                 |
|                     |                     | P+Q     | 21       | 54        | 886      | 2816      | 0.710379                        |   |
|                     |                     | K-F     | 264      | -         | 160      | -         | 0.729277                        |   |
| Nages gneiss        | R6 (96.9 m)         | TR      | 157      | -         | 241      | -         | 0.717688                        | 0.71975                                 |
|                     |                     | K-F     | 222      | -         | 592      | -         | 0.713817                        |   |
|                     |                     | B       | 206      | -         | 193      | -         | 0.72217                         |   |
|                     |                     | C       | 117      | -         | 168      | -         | 0.71759                         |   |
| Cipolin marble      | R6 (149.1 m)        | TR      | 34       | -         | 1937     | -         | 0.708719                        | -                                       |
|                     |                     | C1      | 14       | -         | 2283     | -         | 0.708567                        |   |
|                     |                     | C2      | 89       | -         | 1834     | -         | 0.709179                        |   |

839 TR: total rock sample; P+Q: plagioclase + quartz; K-F: K-feldspar ; B: biotite; C: calcite; C1: light calcite; C2: dark  
840 calcite.

841 Rb\* and Sr\* contents are corrected from the quartz proportion of the sample.

842  $^{87}\text{Sr}/^{86}\text{Sr}$  W-model means the  $^{87}\text{Sr}/^{86}\text{Sr}$  of water in theoretical equilibrium with the rock

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